ON THE RAMAN SPECTRA OF MONOMERIC ACRYLONITRILE IN LIQUID AND SOLID STATES AND INFRARED SPECTRA OF THE POLYMER

N. K. ROY*

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE, CALCUTTA-32

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Plate VIII

ABSTRACT The Raman spectrum of monomeric acrylonitrile solidified and cooled down to −180°C has been recorded and compared with that obtained for the substance at room temperature and the spectra of the monomer in liquid and solid states have been compared to the infrared spectra of the monomer and the polymer. It is found that when the monomer is solidified and cooled to −180°C all the frequencies due to stretching vibrations of the molecule remain unchanged but most of the frequencies corresponding to deformation vibrations shift to longer wave numbers. Further, four new low frequency lines at 51, 81, 96 and 128 cm^{-1} appear in the Raman spectrum of the frozen monomer at −180°C.

It is pointed out that the frequencies 86 and 128 cm^{-1} appear also in the infrared spectrum of the polymer with reversed intensity ratio and it is concluded that these lines and bands are due to oscillations in the molecules associated to each other through N ... H bond. It is further pointed out that the increase in the frequencies of vibrations involving bending of the C–H bonds in the frozen monomer as well as in the polymer further corroborates such a hypothesis.

The appearance of the infrared bands at 1612, 1656 and 2030 cm^{-1} are attributed to the formation of both linear and bent C = C = N chains in the polymer.

INTRODUCTION

The Raman and infrared spectra of monomeric acrylonitrile have been investigated by many workers (Timm and Mecke, 1935, Kohlrausch *et al.*, 1937, Rietz *et al.*, 1938; Thomson and Torkington, 1944, Halverson *et al.* 1948) and some of them (Thomson and Torkington, 1944; Halverson *et al.*, 1948) have assigned the observed Raman shifts and infrared absorption bands to different modes of vibration of the molecule. Liang and Krimm (1958) studied the infrared spectrum of a thin sheet of polyacrylonitrile and made assignments of the observed infrared absorption bands to the different modes of vibration of the constituent groups in the structural unit of the polymer. Recently, Chen *et al.* (1960) obtained polyacrylonitrile by X-ray irradiation of acrylonitrile at 78.5°C and studied the infrared spectrum of the polymer. They reported a new band at

* Present address: Assistant Professor of Physical Chemistry, National Dairy Research Institute, Karnal, Punjab.

2030 cm^{-1} and attributed it to the formation of ketenimine groups C=C=N during polymerisation. They also reported other bands at 1525, 1630, 1675 cm^{-1} the origin of which could not be explained by them. Likewise, Deichert and Tobin (1961) studied the infrared spectrum of polyacrylonitrile formed by passing electric discharge (20000 volts, 60 cycles) through liquid acrylonitrile and observed a band at 2019 cm^{-1} which was attributed to the presence of ketenimine group in the polymer. On the other hand, Liang and Krimm (1958) did not observe any a band either at 2019 cm^{-1} or at 2030 cm^{-1}. It would therefore, be of interest to polymerise the monomer under known conditions and to find out whether the C=C=N chain is formed in the polymer under such conditions.

In two earlier communications (Roy, 1953, 1954) it was pointed out that the changes observed in some of the vibrational frequencies of the monomers with solidification and cooling down to −180°C were to some extent parallel to the changes observed with polymerisation of the monomer. It was, therefore, thought worthwhile to make a comparative study of the changes in the vibrational frequencies of monomeric acrylonitrile with solidification and with polymerisation. With this object the Raman spectra of monomeric acrylonitrile in the solid state at −180°C and the infrared spectrum of the polymer in nujol mull have been studied and compared with the spectra of the monomer in the liquid state. The results obtained have been discussed in the present paper.

EXPERIMENTAL

A sample of monomeric acrylonitrile supplied by the National Chemical Laboratory of India was purified by a method described earlier (Roy, 1953). The purified liquid was fractionated and the distillate obtained at 77.3°±0.5°C was redistilled in pyrex double bulbs under reduced pressure. The Raman spectrum of the purified monomer in the liquid state was studied in the usual way and in the case of the monomer in solid state at −180°C the method used earlier (Roy, 1953) was adopted. A Fuess glass spectrograph having a dispersion of 11 A./mm in the 4046 A region was used to photograph all the Raman spectra and on each spectrogram iron arc spectrum was photographed for comparison. After each exposure proper test for the detection of the presence of polymer in the monomer was applied and by trial the spectrogram of the specimen showing no trace of polymer after exposure was obtained.

Polymeric acrylonitrile was prepared in the laboratory from the purified sample of the monomer. About 0.1% of benzoyl peroxide was used as a catalyst in one sample. This sample was heated in an electric oven at 100°C for about 24 hours when the polymer was obtained as a white powder. Another sample was prepared with a redox catalyst of potassium permanganate and oxalic acid in aqueous suspension of acrylonitrile. The resulting polymer was washed several times with hot water and dried thoroughly by heating under vacuum at

40°C and subsequently in a vacuum desiccator. The samples obtained by these two methods were opaque and consequently their Raman spectra could not be studied. Infrared spectra of the polymer in nujol mull were recorded with and without compensation cell in the reference beam. The former spectrum was used to correctly identify the bands due to the polymer in the regions where nujol has its own absorption bands and in the latter case a thicker film was used to record very weak absorption bands of the polymer in the region where nujol has no band of its own. A 0.022 mm thick cell obtained between two rock salt plates was used to record the infrared spectra of the monomer. A Perkin-Elmer Model 21 infrared spectrophotometer provided with rock salt optics was used for recording the infrared spectra of the samples of monomeric and polymeric acrylonitrile.

RESULTS

The Raman shifts of monomeric acrylonitrile in the liquid and solid states together with the wave numbers (in cm^{-1}) of the infrared bands are given in Table I which also contains the Raman shifts along with their assignments given by Halverson *et al.* (1948). In Table II the frequencies of the infrared absorption

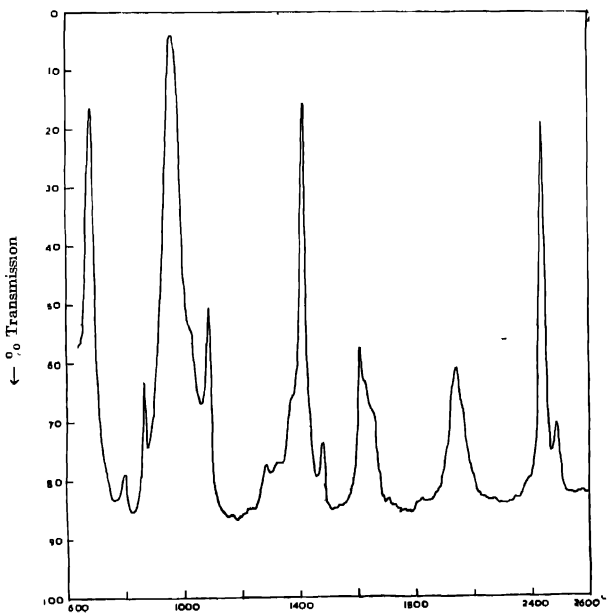


Fig. 2. Infrared spectrum of acrylonitrile monomer (liquid at 27°C)

bands of the polymer obtained after necessary corrections from calibration chart have been tabulated and a probable assignment of the frequencies have been given. Some of the important infrared bands of thin sheet of polyacrylonitrile reported by Liang *et al.* (1958) have also been included in Table II.

Some of the Raman spectra of the monomer are reproduced in Fig. 1, Plate VIII, while the infrared curves of the monomer and the polymer are shown in Figs. 2 and 3.

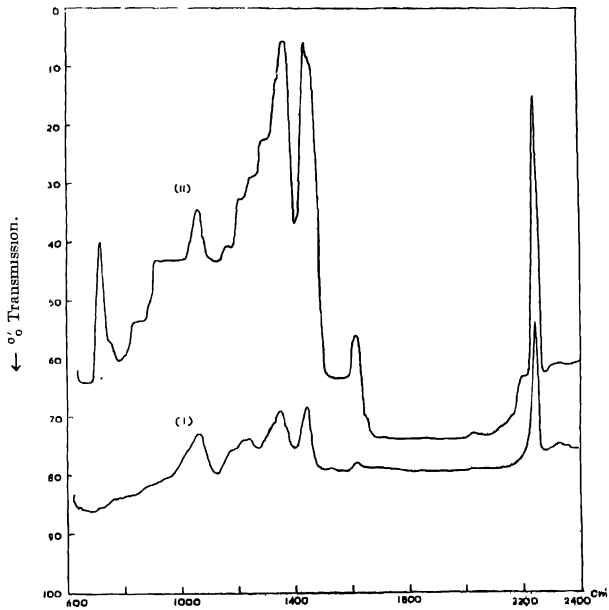


Fig 3. Infrared spectra of polyacrylonitrile in nujol mull
(i) With compensation (ii) Without compensation.

DISCUSSION

(a) *Raman and infrared spectra of monomeric acrylonitrile*

It can be seen from Table I that out of the fifteen vibrational frequencies expected from the molecule of monomeric acrylonitrile thirteen have been observed in the Raman spectrum of the liquid. Previous workers variously reported a weak Raman line in the region 305 cm^{-1}—384 cm^{-1}, but no such line has been observed in the present investigation. When the monomer is solidified and cooled to —180°C all the frequencies due to various stretching vibrations remain unchanged

TABLE 1

Raman shifts and infrared frequencies of acrylonitrile

Infrared frequencies ν, cm^{-1} Liquid at 25°C Present author	Raman shifts $\Delta\nu$, cm^{-1} Liquid at 30°C	Solid at −180°C	Liquid Halverson *et al* (1948)	Probable assignments Halverson *et al.* (1948)
		51 (0)		
	A wing upto 100 cm^{-1} from the Rayleigh line	81 (3b)		
		96 (4b)		
		128 (0)		
	241 (6b)	247 (5)	P 242 (16)	C–C ≡ N bend, a'
			362	C–C ≡ N bend, a''
	568 (1)	568 (0)	P 570 (4.1)	C = C–C bend, a'
682 vs	689 (0)	694 (1)	D 688 (3.0)	C = C torsion, a'
745 w (h)				
800 w				
868 m	874 (1)	874 (1)	P 871 (4 7)	C–C stretch, a'
962 vs				
972 vs (h)	970 (0,vb)	976 (0)	D 970 (2 8)	H_2C C wag, a''
		996 (1)		HRC C wag, a''
1030 m (h)				
1092 m	1093 (0,vb)	1093 (0)	D 1094 (2 8)	CH_2 rock, a' (in plane wag)
1283 m	1287 (2)	1300 (2b)	P 1286 (14)	CH rock, a' (in-plane wag)
1325 wv				
1375 w (h)				
1419 vs	1415 (5)	1426 (4)	P 1412 (20)	CH_2 def, a'
1608 ms	1608 (9)	1608 (8)	P 1607 (36)	C = C stretch, a'
1625 m				682+962*
1653 m				682 + 972
1940 m				962 + 972
2230 vs	2228 (10)	2228 (10)	P 2228 (100)	C ≡ N stretch, a'
2277 w				868 + 1416
	2989 (1)	2989 (1)	P 2989	
	3031 (6)	3031 (6)	P 3032 (45)	C–H stretch, a'
			3068 (7.5)	C–H stretch, a'
	3117 (3)	3117 (3)	P 3116 (14)	C–H stretch, a'

P = Polarised; D = Depolarised
* Assignment proposed now.

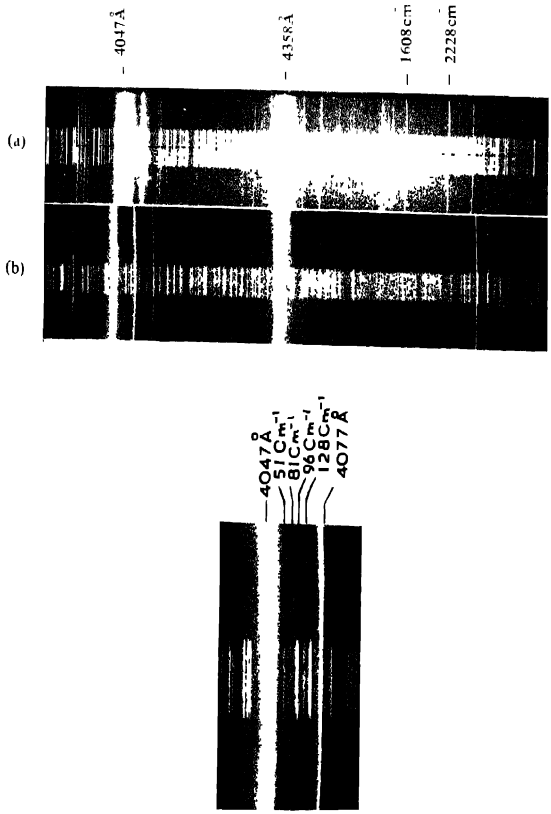


Fig. 1. Raman spectra of acrylonitrile monomer
(a) Liquid at 30°C
(b) Solid at —180°C
(c) Solid at —180°C (showing low frequency lines)

TABLE II

Infrared frequencies (ν, cm^{-1}) of polyacrylonitrile in nujol mull

Of thin film, Liang and Krimm (1958)	In nujol mull	Probable assignment
86 mw		
127 vs		
259 ms		
430 w		
532 m		
675 w		
778 m	760 m (h)	
862 vw	825– 872 m (vvb)	
1041 (sh)	905–1020 ms (vvb)	
1073 s	1058 s	
1115 (sh)	1080 ms (h)	–C–C–C–skeleton vibration of polymer chain
1175 (sh)	1170 ms (b)	
1227 mw	1205 s (b)	C–H bending in the polymer chain
1247 s	1242 s	
1310 w	1310 s (b)	C—H rock
1359 ms	1350 vs (h)	C—H bending in the polymer chain
1375 (sh)	1362 vs	
1447 vs	1440 vs	CH_2 def.
1613 m	1612 m	Symmetric stretching vibration in bent C – C = N group
1678 w	1656 w (h)	Antisymmetric stretching vibration in bent C = C = N group
	2030 vvw	Linear C = C = N stretch
2185 vw	2196 m (bh)	1242+954
2237 vs	2245 vs	C = N stretch
2510 vw		
2810 vw	The bands due to C–H stretching vibrations are overlapped by those due to nujol.	
2870 m		
2940 vs		
2985 (sh)		

but most of the frequencies corresponding to deformation vibrations undergo changes. For instance, the Raman line 970 cm^{-1} of the liquid is split up into two components in the case of the solid at 976 and 996 cm^{-1} respectively. This line is due to wagging of CH_2 and CH groups (Halverson, 1948). The medium strong Raman line 241 cm^{-1} probably due to C—R bending, where R represents $C \equiv N$, shifts to 247 cm^{-1}. Also, the frequency of the Raman line 689 cm^{-1} (682 cm^{-1} in the infrared spectrum) assigned to $C - C$ torsional vibration increases to 694 cm^{-1}, whereas the line 1287 cm^{-1} due to C—H rocking motion shifts to 1300 cm^{-1}. Similarly, the Raman line due to scissoring deformation of the CH_2 group has a frequency of 1415 cm^{-1} in the liquid but increases to 1426 cm^{-1} in the case of the solid. The weak Raman lines 568 and 1093 cm^{-1} do not show any shift although these lines are assigned to $C \equiv C-C$ bending and CH_2 rocking motions respectively. The changes mentioned above may be due to formation of a weak linkage between the H atom of the CH_2 groups and the N atom of the neighbouring molecule. Probably this N...H bond lies in the plane containing the $C \equiv N$ and H- C bonds so that any bending of the C—H group at right angles to the plane results in the bending of the weak linkage and it affects very little the frequency of the CH_2 rocking vibration. Similarly, the weak linkage does not alter the bending oscillation frequency of the $C \equiv C$—C group.

It is observed that in the present case the $C = C$ stretching vibration frequency, 1608 cm^{-1}, is lower than that in ethylene (Herzberg, 1945), styrene (Roy, 1954) or methyl methacrylate (Roy, 1953). Also the $C \equiv N$ frequency, 2228 cm^{-1}, is lower than that observed in the spectra of other simple nitriles, e.g., succinonitrile, methyl cyanide, etc. (Herzberg, 1945). The conjugation between $C = C$ and CN bonds in the structure, $C = C- C \equiv N$, of acrylonitrile molecule seems to be responsible for the lowering of both the frequencies. This will also increase the electronic charge on the terminal C and N atoms and facilitate the formation of intermolecular N...H bonds mentioned earlier.

Besides the changes discussed above, other characteristic changes also occur in the Raman spectrum with solidification. Four new Raman lines of frequency shifts 51, 81, 96 and 128 cm^{-1} are observed in the spectrum of the solid at −180°C. Of these, the two Raman lines at 81 and 96 cm^{-1} are fairly intense, while the other two lines are weaker. These lines are evidently not due to intramolecular vibrations.

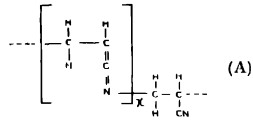
It may be pointed out that although two bands at 86 and 127 cm^{-1} were observed by Liang and Krimm (1958) in the infrared spectrum of polyacrylonitrile there are no corresponding lines in the Raman spectrum of the liquid monomer, because the intensity of the wing present upto 100 cm^{-1} the Rayleigh line in the Raman spectrum of the liquid monomer is very feeble in the above two regions. The strong new Raman lines 81 and 96 cm^{-1} observed in the case of frozen monomer

may correspond to the feeble infrared band at 86 cm^{-1} and the Raman line 128 cm^{-1} may correspond to the infrared band at 127 cm^{-1}. Thus it appears that in the polymer also the weak N...H bond is formed and the vibration of low frequencies observed in the case of the frozen monomer occurs also in the polymer. Liang and Krimm (1958), however, concluded that no hydrogen bonding takes place in the polymer, but they seem to have overlooked the fact that the C ≡ N stretching frequency may not be affected even if the N.. H bond is formed, as pointed out earlier. The assignment of the two frequencies 86 and 127 cm^{-1} made by them may not therefore be correct.

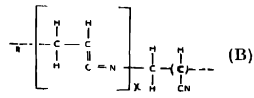
The number of new low frequency lines is generally large in substituted ethylene when at least one of the substituents has non-bonding electrons or a resonance structure as in benzene. In the present case there may be more than one molecule in the unit cell and the strengths of the N...H bonds formed between neighbours at different distances may be different. The assignment of the low frequency lines to oscillation of N ..H groups is supported by the facts that in the case of tetrachloroethylene at −180°C no new low frequency Raman line is observed, while frozen trichloroethylene shows one such line at 62 cm^{-1} (Sanyal, 1950).

Infrared spectrum of polyacrylonitrile

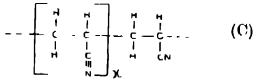
It is seen from Table II that in the infrared spectrum of polyacrylonitrile in nujol mull there are extra bands at 1058, 1170, 1205, 1242, 1350, 1656, 2030 and 2196 cm^{-1} which are not represented in the infrared spectrum of the monomer In order to account for these bands one has to explain first the appearance of two frequencies 1612 and 1656 cm^{-1} in the spectrum of the polymer. Evidently, although in the usual process of polymerisation the C = C bond should be replaced by the C—C, in this case in some percentage of the polymer the C = C reappears, and therefore, an alternative process takes place. The formation of the ketenimine group has been suggested by Chen *et al* (1960). The characteristic frequency of linear C = C = NH group is 2030 cm^{-1}, but when the angle between C=C and C = N is about 90° the group may have the two frequencies 1612 and 1656 cm^{-1} respectively due to the symmetric and antisymmetric vibrations. As all the three frequencies have been observed in the present case it is evident that in certain percentage of the polymer the ketenimine chain is linear, in some it is bent and in the rest no ketenimine chain is formed. The three cases are illustrated by the formulae (A), (B) and (C). It may be pointed out here that Chen *et al.* (1960) observed the bands 1630 and 1675 cm^{-1} but overlooked this plausible explanation of their origin. On the other hand, Liang and Krimm (1958) observed only the two bands 1613 and 1678 cm^{-1} but not the band 2030 cm^{-1}. Hence in their polymer also the bent group C = C = N was formed but the linear ketenimine chain was not formed. The bands observed by them was due to this configuration of the polymer and not due to impurities as assumed by them.



(A)



(B)



(C)

Of the remaining extra bands the bands 1058 and 1170 cm^{-1} can now be assigned to the vibration of the chain C—C—C C in the predominant configuration of the polymer and the bands 1205, 1242 and 1350 cm^{-1} may be due to vibration of the C—H groups in the chain involving C—H bond.

It may be pointed out that the infrared bands 1310 and 1440 cm^{-1} of the polymer correspond to the bands at 1283 and 1416 cm^{-1} respectively of the monomer and the increase in the values indicates formation of N...H bonds in the polymer. The band 2196 cm^{-1} is rather weak and it may be due to the combination of the frequencies 1242 and 954 cm^{-1}.

As mentioned earlier, the frequency 86 cm^{-1} observed in the infrared spectrum of the polymer is replaced by two frequencies 81 and 96 cm^{-1} in the Raman spectrum of the frozen monomer, while the frequency 128 cm^{-1} appears in the Raman spectrum of the frozen monomer as well as in the infrared spectrum of the polymer. The intensities are however reversed in the two spectra, which shows that these are due to some fundamental vibrations in which the selection rule is operative so that the Raman lines 81 and 96 cm^{-1} are very intense while the infrared band 86 cm^{-1} is weak. These Raman lines have been assigned to vibrations in molecules of the frozen monomer associated to each other through N...H bonds. Evidently, in the polymer also such hydrogen bonding takes place. The low frequency Raman lines are therefore not produced by the crystal lattice because in the polymer there is no such regular arrangement.

It may be pointed out that the unusual properties of polyacrylonitrile, viz., that the polymer is an opaque powder while polystyrene and polymethylmethacrylate are transparent, that polyacrylonitrile is infusible even upto a temperature of 250°C, that it is insoluble in common polymer solvents, but dissolves only in some special solvents, e.g., succinonitrile, dimethylformamide etc., may be due to the abnormal ketonimine type of linkage at least in some percentage as well as N...H type of linkage present in the polymer as discussed above.

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